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(54) Title: CROSS-LINKED POLYKETONES (57) Abstract <p>A process for cross-linking a polyketone polymer comprising exposing the polyketone polymer to high energy radiation; and a cross-linked polyketone which is obtainable by said process.</p>			

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CROSSLINKED POLYKETONES

This invention relates to polyketone polymers. More particularly, this invention relates to crosslinked polyketone polymers, their production and their application.

5 Linear alternating polymers of carbon monoxide and olefins herein referred to as polyketones or polyketone polymers are well known in the art. This class of polymers is disclosed in numerous patent documents, such as in US-A-4880865 and US-A-4818811.

10 Polyketone polymers display a well balanced set of mechanical properties which make them particularly useful as engineering thermoplastics. The excellent properties of polyketones could be further exploited by improving the materials so that they exhibit improved tribological properties. Parts and items made from such improved materials would be able to resist wear and to bear greater frictional loads when in rolling or sliding contact, in particular over extended durations. Such properties are generally attained through the addition of 15 additives. However, it would be beneficial if they could be attained without the addition of additives to avoid other changes in the polyketone properties due to additive loading of the polymer matrix. It would also be beneficial if other attributes such as thermal 20 performance, dimensional stability and tensile strength could be improved without further loading the polymer with additives.

25 It is known that polymers containing ketone groups degrade according to Norrish type I and/or Norrish type II scission reactions upon exposure to UV radiation. 30 This occurs either in the presence or absence of oxygen.

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When UV irradiated in the presence of oxygen the polyketones undergo significant molecular weight loss resulting in a polymer having undesirable properties such as brittle behaviour and loss of mechanical strength.

5 It is known that polyketones can undergo crosslinking in the melt. The crosslinked materials so obtained suffer from a loss in ductility and toughness, they often possess discrete gel particles in the polymer matrix and they exhibit a reduced crystallinity and/or a reduced
10 crystalline melting point. Furthermore, such materials are destabilized toward oxidative degradation. In short, polyketones which are crosslinked in the melt are not particularly desirable e.g. in applications as an
15 engineering thermoplastic. Aside from chemical modification, substantially crosslinked polyketones which do not exhibit such a loss in mechanical properties have not yet been produced.

US-A-3812025 proposes crosslinking by high-energy radiation of polyolefins having a small mole fraction of ketone groups in the backbone or in side chains, viz. generally less than about 10 mole%, in particular less than about 5 mole%, calculated on monomer. These ketone groups are incorporated by copolymerizing the olefin with carbon monoxide or with a vinyl ketone, optionally by graft or block copolymerization. Only polymers with a low content of ketone groups have been employed because, according to US-A-3812025, these polymers have all the desired properties of unmodified polyolefins. While the possibility of crosslinking polyolefins with up to 25 50 mole% ketone groups is also presented, such crosslinking would be expected to be accompanied by Norrish I/II chain scission reactions. The inventor of US-A-3812025 explains in J.A. Slivinskas and J.E. Guillet, " γ -Radiolysis of Ketone Polymers", Journal of Polymer Science, Vol. II, 3043-3056 (1973) why this is
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so. There he states that the photolysis attributable to Norrish type I and Norrish type II reactions increases with decreasing aliphatic/ketone lengths, i.e. with greater content of ketone groups. This view would be in accordance with the understanding of the degradative processes set forth above. Thus, this work suggests that irradiated polyketones should undergo simultaneous scission and crosslinking resulting in a crosslinked material which would not retain ductility, impact and tensile strength. Any crosslinked material so formed would be expected to be comprised of relatively low molecular weight fragments. Thus, it can be seen why the claims of US-A-3812025 are restricted to crosslinking by high-energy radiation of polymers having a large aliphatic chain length to the ketone portion of the polymer molecules. The working examples of the patent are drawn to materials having a maximum of less than 10 mole% ketone groups.

Thus, the prior art would suggest that by high energy radiation polyketone polymer would undergo degradation by chain scission. It has now surprisingly been found that the properties of polyketone polymers can be enhanced through curing by high energy radiation and that the materials produced by this process are unique in their properties, such as in enhanced thermal and mechanical properties, for example toughness, and in tribological characteristics, for example wear. Hence, the products are excellently suitable for use in a range of highly demanding applications, for example applications where articles of the radiated polyketones are placed in rolling or sliding contact with each other or with other articles.

Accordingly, the invention relates to a process for crosslinking a polyketone polymer comprising crosslinking

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the polyketone polymer by exposure to high energy radiation.

The invention further relates to the crosslinked polyketone polymer per se as obtainable by the process of the invention. The invention also relates to articles of manufacture which comprise the crosslinked polyketone of this invention and/or which can be obtained by a process which includes the process for crosslinking a polyketone in accordance with this invention. The processes of this invention comprise irradiating polyketone polymer at one or more points during the processing of the polymer or of articles made therefrom. The invention also includes compositions comprising a crosslinked polyketone according to the invention.

The following terms when used in this specification, some of which are tribological terms, shall have the following meanings:

As indicated hereinbefore, polyketones or polyketone polymers are linear alternating polymers of carbon monoxide and at least one ethylenically unsaturated hydrocarbon. These terms refer to copolymers, terpolymers, quaterpolymers etc. of these monomers. Polymer additives well known in the art can be used in conjunction with the polyketones. For instance, fillers, extenders, lubricants, pigments, plasticizers, and other polymeric materials can be added to the polyketone compositions to improve or otherwise alter the properties of the compositions.

"DCOF": During relative motion of two surfaces in contact the DCOF is the ratio of the resulting frictional force to the applied normal force while holding the relative surface velocity constant over time.

"LPV": While holding the relative surface velocity constant between two specimens in contact and increasing the applied normal force in a stepwise manner in time,

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the LPV is the multiplicative product of the normal pressure and surface velocity at the step just prior to catastrophic material failure due to thermal softening.

5 "Wear K Factor": As performed on a thrust washer test apparatus using ASTM D3702 and defined as:

$$K \text{ (wear factor)} = \frac{W}{FVT},$$

where: W = volume wear (m^3), F = normal force (N), V = relative surface velocity (m/s), and T = testing time (h)

10 "Crosslinking" is the attachment of two or more polymer molecules at least one point on the backbone of each polymer molecule so joined. Crosslinking results in an increase in molecular weight. Extensive crosslinking results in the formation of a gel which comprises a network of polymer chains rendering the gel insoluble in 15 solvents used for dissolving the uncrosslinked polymer. A crosslinked polyketone is typically a polyketone polymer which exhibits an increase in the weight average molecular weight of at least 10% relative to the polyketone starting material. Indeed, polyketone polymer 20 which is already crosslinked to one degree or another can be further crosslinked according to the method of this invention.

25 "Curing" is the treatment of the polyketone polymer in accordance with this invention. Herein the polyketone polymer is crosslinked without an overall loss in useful mechanical properties. As indicated hereinafter, cured polyketone polymers are distinguished from other crosslinked polyketone polymers (e.g. those crosslinked in the melt) in their exhibition of substantially no 30 increase (relative to the uncured material from which it was made) in the intensity of emission at 490 nm when excited with 400 nm light. Typically there is less than 10% increase in the intensity in emission at 490 nm.

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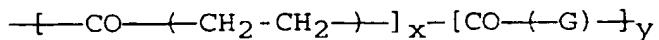
"Specific surface area" means the surface area per unit mass (m^2/g). It is a relative measure of the amount of the volume of a given material which is presented as surface area.

5 The polyketones for use in this invention are linear alternating copolymers of carbon monoxide and at least one ethylenically unsaturated compound. Thus, the polyketone polymers are of a linear alternating structure which means that they contain one molecule of carbon
10 monoxide for each molecule of the ethylenically unsaturated compound. Ethylenically unsaturated compounds comprise suitably up to 20 carbon atoms and include compounds which consist exclusively of carbon and hydrogen and compounds which in addition comprise hetero atoms, such as unsaturated esters, ethers and amides.
15 Unsaturated hydrocarbons are preferred. Examples of suitable ethylenically monomers are aliphatic α -olefins, such as ethene, propene and butene-1, cyclic olefins such as cyclopentene, aromatic compounds, such as styrene and α -methylstyrene and vinyl esters, such as vinyl acetate and vinyl propionate. The preferred polyketone polymers are linear alternating copolymers of carbon monoxide and ethene or linear alternating copolymers of carbon monoxide, ethene and another ethylenically unsaturated compound of at least 3 carbon atoms, particularly an α -olefin such as propene or butene-1.
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When the preferred polyketone polymers of carbon monoxide, ethene and another ethylenically unsaturated compound are employed, there will be within the polymer typically at least 2 units incorporating a moiety of ethene for each unit incorporating a moiety of the other ethylenically unsaturated compound(s). Preferably, there will be from 10 units to 100 units incorporating a moiety of ethene for each unit incorporating a moiety of the other ethylenically unsaturated compound(s). The polymer
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chain of preferred polyketone polymers is therefore represented by the repeating formula



where G is the moiety of the ethylenically unsaturated compound of at least 3 carbon atoms polymerized through the ethylenic unsaturation and the ratio of y:x is typically no more than 0.5. When linear alternating polymers of carbon monoxide and ethene are employed in the compositions of the invention, there will be no second ethylenically unsaturated compound present and the polymers are represented by the above formula wherein y is zero. When y is other than zero the $-\text{CO---CH}_2\text{-H}_2\text{---}$ units and the $-\text{CO---G---}$ units are found randomly throughout the polymer chain, and preferred ratios of y:x are from 0.01 to 0.1. The precise nature of the end groups does not appear to influence the properties of the polymer to any considerable extent so that the polymers are fairly represented by the formula for the polymer chains as depicted above.

The polyketone polymers of number average molecular weight from 1000 to 200,000, particularly those of number average molecular weight from 20,000 to 90,000 as determined by gel permeation chromatography are of particular interest. A preferred range of the weight average molecular weight is from 2000 to 1,000,000, in particular from 40,000 to 500,000. The physical properties of the polymer will depend in part upon the molecular weight, whether the polymer is based on a single or on a plurality of ethylenically unsaturated compounds and on the nature and the proportion of the ethylenically unsaturated compounds. Typical melting points for the polymers are from 175 °C to 300 °C, more typically from 210 °C to 270 °C, as determined by

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5 differential scanning calorimetry. The polymers have typically a limiting viscosity number (LVN), measured in m-cresol at 60 °C in a standard capillary viscosity measuring device, from 0.5 dl/g to 10 dl/g, more typically from 0.8 dl/g to 4 dl/g.

10 Preferred methods for the production of the polyketone polymers are known from US-A-4808699 and US-A-4868282. US-A-4808699 teaches the production of polyketone polymers by contacting ethene and carbon monoxide in the presence of a catalyst comprising a Group VII metal compound, an anion of a nonhydrohalogenic acid with a pKa less than 6 and a bidentate phosphorus, arsenic or antimony ligand. US-A-4868282 teaches the production of polyketone polymers by contacting carbon monoxide and ethene in the presence of one or more hydrocarbons having an ethylenically unsaturated group with a similar catalyst.

15

20 In the process of this invention, the degree or depth of cure is dependent, in part, on the source and intensity of the radiation source. When the material is cured by a photon-type source of radiation such as γ-radiation, the cure can be affected throughout the polymer matrix. This is largely due to the penetrating nature of the radiation. Surface curing will occur with 25 non-penetrating radiation such as an ion beam. Here, the type of ion used and the intensity of the bombardment will dictate the depth and degree of cure. Lighter ions will, of course, create a greater depth of cure than will heavier ions.

30 As another example, electron beam (e-beam) crosslinking is particularly attractive as an industrial application. Polymer wires and cables, pellets, heatshrink products, roto-moulded parts, blow-moulded containers, injected moulded parts, and sheets are all 35 easily subjected to high energy bombardment in such

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off-line processes with a minimum impact on other parts of the manufacturing process. The process can be nearly instantaneous with exposure times measured in seconds. One skilled in the art will readily appreciate that the degree of crosslinking is directly related to the level of e-beam exposure and can be readily controlled.

High energy radiation useful to bring about the cure of this invention is any irradiation which occurs with energy greater than 10 eV, especially greater than 100 eV, and can be successfully undertaken with irradiation which occurs with energy up to 10^9 eV. Particularly useful is an energy level of 10^4 - 10^8 eV. Well known sources of such radiation include e-beam, X-ray, gamma ray, and ion beams. Preferred sources are e-beam, gamma radiation, and, when surface curing is desired, ion beam. The most preferred source is a gamma radiation source such as industrial Co⁶⁰ emitters.

In particular when gamma radiation, such as from a Co⁶⁰ emitter, is used as the source of irradiation preferred doses range between 5 Mrad and 25 Mrad although doses between 1 and 50 Mrad are believed to have a beneficial effect. It is most preferred that the dose be 5-5.6 Mrad. Any rate necessary to apply the doses needed for cure may be applied but cure is believed to be most efficiently affected with the highest rate of irradiation possible for the given emitter. The dose and rate of irradiation can be significantly lowered with the additional use of radiation accelerators known in the art such as triallyl cyanurates, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and allyl methacrylate. Polyketone may be cured with or without the presence of other additives such as antioxidants and melt stabilizers. No special preparation of the polyketones is necessary.

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It has surprisingly been found that tribological properties such as LPV and Wear Factors have been improved through the practice of this invention. In the most preferred embodiment of this invention, the cured polyketone polymer displays an LPV which exceeds the measurement capacity of commercially available analyzers. That is, the LPV is greater than 7000 kPa.m/s (200,000 psi.ft/min). Cured polyketone gears, bearings, and other parts which are in rolling or sliding contact can thus bear greater loads than parts which are not so cured.

High temperature properties of the materials made according to this invention are also improved over those of the prior art. For example, the heat deflection temperature (HDT) of a polyketone sample cured by exposure to 20 Mrad of gamma radiation was increased to 100 °C, whereas a similar uncured polyketone polymer sample displayed an HDT of 92 °C.

It is also believed that long term mechanical properties such as, dimensional stability (e.g. creep), tensile strength and resistance to fatigue are also improved through the practice of this invention as are other properties such as barrier properties, elastic memory, stress crack resistance, resistance to plasticization, puncture/tear resistance, and melt processability of the polymer. For example, cured polyketones made according to this invention should exhibit a lower transmission of reagents through the polymer matrix and should resist swelling or sorption of water, alcohol, chlorinated hydrocarbons and the like relative to uncured polyketones.

The cured polyketones of this invention can be used to produce snap fit parts, parts for use in load bearing applications, and heat shrinkable moulded parts. It should also be useful in the preparation of parts useful

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in down-hole mining applications such as chemical, wear, and heat resistant piping. Sleeves, wire and cable jacketing, coatings, connectors, liners, tubes and the like can also be made to good effect from this material. 5 Such parts would have particular utility in the electrical, automotive, aerospace, and medical industries. Extrusion grade polymers and films can also be made from cured polyketones prepared according to this invention.

10 The crosslinked polyketones produced according to this invention can be readily distinguished from the melt crosslinked materials by characterization according to both visible fluorescence observations and fluorescence spectroscopy (excitation/emission spectra). Melt 15 crosslinked polyketones display visible fluorescence under illumination by a mercury vapour lamp while polyketones crosslinked by exposure to high energy radiation do not. Further, excitation and emission spectra for melt crosslinked polyketone is vastly 20 different from polyketone polymer crosslinked by high energy radiation as is set forth in the examples. Such characteristic differences can only result from 25 differences in chemical structure. Melt crosslinked polyketone polymers have a chemical structure comprising a fluorophore species while irradiation cured polyketone polymers do not, similar to the polyketone polymer starting material from which it was produced.

It is advantageous to restrict the susceptibility of 30 the polyketone polymer to the influence of oxygen to affect cure properly. Namely, conducting the irradiation in the substantial presence of oxygen may result in polymer chain scission and thus low molecular weight materials are produced. By substantial presence of oxygen, it is meant that a significant portion of the 35 total volume of the polymer is exposed to oxygen. The

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specific surface area is a measure of the degree of such exposure when the polymer is irradiated in air. The greater the specific surface area, the greater will be the propensity for chain scission. Polyketones having 5 specific surface areas of less than $2.1 \times 10^{-3} \text{ m}^2/\text{g}$ will undergo predominantly crosslinking while those having specific surface areas of at least $0.10 \text{ m}^2/\text{g}$ will undergo significant chain scission in the presence of air. It is believed that polyketones having specific surface areas 10 of as little as $1 \times 10^{-3} \text{ m}^2/\text{g}$ will crosslink in the presence of air. Thus, for irradiation in the presence of air it is preferred that the specific surface area of the polyketone polymer or an article made therefrom is less than $0.1 \text{ m}^2/\text{g}$ in particular less than $2.1 \times 10^{-3} \text{ m}^2/\text{g}$, 15 most in particular less than $1 \times 10^{-3} \text{ m}^2/\text{g}$. Thus, cryoground polymer is ordinarily less suitable for irradiation crosslinking in the presence of air due to the high proportion of polymer volume which would be exposed to oxygen. However, strands, most finished 20 articles of manufacture such as gears and bearings, stock shapes for further machining, sheet, and the like are ordinarily well suited for irradiation curing.

Conducting the process of this invention in a vacuum or while blanketing the material or fabricated part with an inert gas such as nitrogen or a noble gas can also be used to properly attain curing of the polyketone. 25

The temperature at which this process is carried out does not appear to be important. However, it is preferred that it be conducted at temperatures below the melting point of the polyketone polymer, such as at a 30 temperature chosen in the range of 0-170 °C, in particular 10-150 °C. Curing through the crosslinking of finished parts is one such preferred process. Nevertheless, curing can still be conducted above the

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melting point to produce various useful embodiments of the cured material.

The invention is further illustrated through the following non-limiting examples.

5 EXAMPLES

In each of the examples, properties were determined as follows.

Mechanical Properties were tested using ASTM D638, 3.18 mm (1/8") thick Type I and Type V tensile bars.

10 Type I tensile bars were tested at a strain rate of 50.8 mm (2 inch) per minute with a 114 mm (4.5 inch) grip to grip distance. Strain rates of 12.7 mm (0.5 inch) per minute and grip to grip distance of 25.4 mm (1.0 inch) were used for Type V bars.

15 The Molecular Weight was determined using a GPC system equipped with a Phenomenex Phenogel 7.8 mm X 30 cm, 5 μm linear and Phenogel 5 μm , 500 Å columns connected in series. Hexafluoroisopropanol was used as the solvent with 0.01 M ammonium trifluoroacetate as modifier. The system was equipped with a refractive index detector and a mini-DAWN light scattering detector.

20 Tribological Properties were measured using a Computer Controlled Multi-Specimen Test Machine. In this testing, a thrustwasher injection moulded from the material to be tested was spun against a steel stationary washer in one direction. Data logging for the following parameters was conducted continuously: speed, load, temperature, wear, and run time. LPVs, DCOF, and Wear Factors were computed from this data logging.

25 30 LPV was measured at 0.51 m/s (100 fpm) velocity with stepped 4.4 N (10 lb) load increments from 9.1 N (20 lb) to specimen failure. Specimen failure is the sudden loss of structural integrity at melt softening. Wear tests were run at 2.41 MPa (350 psi) load and 0.28 m/s (56 fpm) velocity for 4 hours to seat test specimens which were

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not irradiated. Specimens which were then irradiated (after seating) were run at 0.28 MPa (40 psi) and 0.25 m/s (50 fpm) for 20 hours on a new stationary washer (a 1018 carbon steel with a 16-18 rms finish). The test specimen and stationary washer were measured for thickness and weight before and after each run. The specific gravity of the test specimen was then incorporated into the computation of the resulting wear factor.

Heat Deflection Temperatures (HDT) were determined using ASTM D648 with a 1.82 MPa (264 psi) load. Melting point (T_m) and enthalpy of fusion (ΔH) were determined under nitrogen using a differential scanning calorimeter (model 7700) with a ramp rate of 20 °C per minute.

Unless otherwise stated, irradiation of the materials used in the examples was accomplished by subjecting the polyketone polymer with a Co^{60} γ -radiation source at a rate of 0.28 Mrad/hour.

Example 1

Neat linear alternating polyketone (terpolymer of carbon monoxide, ethylene, and a minor amount of propylene) having a melting point of about 220 °C and a limiting viscosity number of 1.8 dl/g was prepared. This material was blended with 0.2% IRGANOX 1330 (IRGANOX is a trademark) hindered phenol antioxidant, 0.3% NUCREL 535 (NUCREL is a trademark) ethylene methacrylic acid copolymer and 0.2% calcium hydroxyapatite (all percentages are as a weight percent of total weight of the mixture). Tensile bar specimens were prepared from this material. Specimen A was not subsequently irradiated. Specimens B and C were γ -irradiated in air with 5.6 Mrad and 20 Mrad, respectively. Various mechanical properties and characteristics were measured as set forth in Table 1 below.

Table 1

Tensile Bar	Molecular Weight (Mw)	ΔH J/g	Yield Strain, %	Yield Stress, MPa (psi)	Break Strain, %	Break Stress, MPa (psi)	Notched Izod J (ft-lb)	HDT °C	Tm °C
A*)	69,400	70	23	61.0 (8853)	308	101.2 (14,677)	6.7 (4.9)	92	224
B	150,000	70	24	61.9 (8974)	311	102.8 (14,916)	6.1 (4.5)	Not Tested	222
C	70% GEL	Not Tested	25	64.6 (9364)	265	95.3 (13,824)	5.3 (3.9)	100	Not Measured

*) For comparison

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This example shows that γ -irradiation of polyketone polymer results in a molecular weight increase and that such increase is related to the dosage of radiation (network formation occurred at 20 Mrad). Further, the 5 cured polyketones according to this invention maintain or improve the excellent tensile strength and ductile properties of the polymer, as measured by Notched Izod impact testing. High temperature properties are also improved. The crystallinity of the polymer is not 10 affected by the cure process.

Example 2

Neat linear polyketone (terpolymer of carbon monoxide, ethylene, and a minor amount of propylene) having a melting point of about 220 °C and a limiting 15 viscosity number of about 1.8 dl/g was prepared (Mw of 83,000 with a MWD of 4.3). This material was blended with 0.5% IRGANOX 1330 hindered phenol antioxidant in a twin screw extruder and forced through a die to yield a 1.52 mm (60 mil) (diameter) strand. Approximately 20 10 grams of the polymer strand was placed in a glass tube in the presence of air. The sample thus presented a specific surface area of about $2.1 \times 10^{-3} \text{ m}^2/\text{g}$. No evacuation or blanketing of the atmosphere was conducted. The sample was then exposed to 5.6 Mrad of γ -radiation. 25 The weight average molecular weight (Mw) of the polymer was then analyzed and found to be 160,000 with a molecular weight distribution (MWD) of 11.3. This increase in Mw indicates that curing has occurred.

Example 3

The polyketone polymer of Example 2 was cryoground 30 into a powder. About 10 grams of the polymer powder was placed in a glass tube which was evacuated to reach a pressure of 0.4 Pa (3 mtor). The samples thus presented a specific surface area of $0.10 \text{ m}^2/\text{g}$ (as measured by the BET method). The sample was then exposed to 5.6 Mrad of 35

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γ -radiation. The molecular weight (Mw) of the polymer was then analyzed and found to be 170,000 with an MWD of 8.1 indicating that significant curing had occurred.

Example 4

5 The polyketone polymer as set forth in Example 1 was processed through a tubular blown film line using a 31.8 mm (1.25 inch) extruder and prepared as a film having a thickness of 0.051 mm (2 mil). Four 10.2x10.2 cm (4X4 inch) specimens were prepared from the blown film. The first specimen was not irradiated. It 10 was analyzed to determined to have a Mw of 79,400. Three samples were then placed in an Energy Science Incorporated CB 150 Electrocurtain apparatus. The sample chamber was purged with nitrogen such that oxygen content 15 was less than 100 ppm. Specimens were then exposed to electron beam irradiation having a voltage of 165 kv. The cathode power was 360 W. The specimen exposed to a total of 5 Mrad was found to have a Mw of 87,500, the specimen exposed to 10 Mrad was found to have a Mw of 20 141,000, and the specimen exposed to 20 Mrad was found to have a Mw of 144,000 (with 20% gels).

This example shows that e-beam irradiation of polyketone polymer results in the curing of the polymer.

Example 5

25 Three different 3.18 mm (1/8 inch) type I tensile bars were prepared from the polyketone polymer of Example 1. For comparative purposes tensile bar A was not irradiated or treated to a further melt heat history. Tensile bar B was subjected to 5.6 Mrad of γ -radiation. 30 For comparative purposes tensile bar C was placed in a 3.18 mm (1/8 inch) mould and heated for 20 minutes at 265 °C in a compression moulder with a clamp pressure of 70 MPa (10,000 psi) to induce crosslinking in the melt. Tensile bar C was then removed from the compression 35 moulder and cooled to room temperature.

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The tensile bars were then submitted to visible fluorescence observations by exposing them to the light emitted from an unfiltered hand-held mercury vapour lamp. No visible fluorescence was observed in the case of
5 Tensile bars A and B. A bright yellow fluorescence was observed in Tensile bar C, the melt crosslinked sample.

Further fluorescence spectrophotometric characterization was undertaken by studying the excitation and emission spectra of the solid materials at
10 23 °C with a MPF-66 spectrophotometer. Tensile bars A and B showed only faint fluorescent emissions at 490 nm (relative intensity of 0.04) after excitation with light of 400 nm while Tensile bar C showed one broad, intense peak centered at 490 nm (relative intensity of 1.04).
15

This example illustrates that the cured polyketone according to this invention has different molecular structure from the melt crosslinked polyketone.

Example 6

Polyketone polymers prepared in accordance with
20 Example 1 were injection moulded into thrust washers for tribological testing. Comparative specimen A was not subsequently exposed to radiation. Specimen B was irradiated with 5.6 Mrad of γ -radiation and Specimen C was irradiated with 20 Mrad of γ -radiation. Tribological properties were as follows:
25

Specimen A: LPV=1120 kPa.m/s (32,000 psi.ft/min),
Specimen B: LPV>7000 kPa.m/s (> 200,000 psi.ft/min)
(exceeds capacity of instrumentation),
Specimen C: LPV>7000 kPa.m/s (>200,000 psi.ft/min)
30 (exceeds capacity of instrumentation).

This example illustrates the significant improvement in tribological properties exhibited in polyketone polymers cured according to this invention. Typical additive blends of polyketones prepared expressly for tribological applications have been found to have LPVs of
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1860-1930 kPa.m/s (53,000-55,000 psi.ft/min). Thus it can
be seen that there is a substantial improvement in
tribological properties of polyketones subjected to the
curing process of this invention. This improvement was
5 not expected and makes articles produced according to
this invention especially well suited for applications in
which they are to be placed in rolling or sliding contact
with another article. Gears, bearings, cams, followers,
10 sprockets, washers, vessel liners, bushings, pulleys,
sliding plates and many other like articles would benefit
from the curing process.

C L A I M S

1. A process for crosslinking a polyketone polymer comprising exposing the polyketone polymer to high energy radiation.
- 5 2. A process as claimed in claim 1, characterized in that the polyketone polymer is a linear alternating copolymer of carbon monoxide with ethene and optionally another olefinically unsaturated compound of at least 3 carbon atoms.
- 10 3. The process as claimed in claim 1 or 2, characterized in that the polyketone polymer has a specific surface area of less than $2.1 \times 10^{-3} \text{ m}^2/\text{g}$.
4. A process is claimed in claim 1 or 2, characterized in that the process is conducted in an inert atmosphere.
- 15 5. A process as claimed in any of claims 1-4, characterized in that the high energy radiation is γ -radiation.
- 20 6. A process as claimed in any of claims 1-5, characterized in that the high energy radiation is electron beam radiation, ion beam radiation, X-ray radiation or, in particular, gamma radiation.
7. A process as claimed in any of claims 1-6, characterized in that the dose of radiation is between 1 and 50 Mrad, in particular between 5 and 20 Mrad.
- 25 8. A process as claimed in any of claims 1-6, characterized in that an increase of the weight average molecular weight of the polyketone of at least 10%, in particular of at least 100% is effected.
9. A crosslinked polyketone polymer, characterized in that it is obtainable by a process as claimed in any of 30 claims 1-8.

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10. An article of manufacture, characterized in that it comprises a crosslinked polyketone as claimed in claim 9.
11. An article of manufacture, characterized in that it is obtainable by a process which includes a process as claimed in any of claims 1-8.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 96/05730

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C71/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C C08J B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 237 (C-305), 24 September 1985 & JP 60 096623 A (SEKISUI KAGAKU KOGYO KK), 30 May 1985, see abstract ---	1,2,5,6, 9-11
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 390 (C-394), 26 December 1986 & JP 61 176637 A (SEKISUI CHEM CO LTD), 8 August 1986, see abstract ---	1,2,5-7, 9-11
X	FR 2 084 932 A (FARBENFABRIK BAYER) 17 December 1971 see page 6, line 25 - line 33; claims 1,3 ---	1,5,6, 9-11
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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- *O* document referring to an oral disclosure, use, exhibition or other means
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- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *&* document member of the same patent family

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Date of the actual completion of the international search Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 96/05730

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 238 447 A (CIBA GEIGY AG) 23 September 1987 see abstract see claims 1,3-5,10 ---	1,6,7, 9-11
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 195 (C-1049), 16 April 1993 & JP 04 342739 A (IDEMITSU KOSAN CO LTD), 30 November 1992, see abstract ---	1,4,6, 9-11
A	US 3 812 025 A (GUILLET J) 21 May 1974 cited in the application -----	1

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Information on patent family members

Inte onal Application No

PCT/EP 96/05730

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